Research Article

Concerning the Problem of Searching for the Optimal Palladium Cathode

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Abstract

This article attempts to describe the processes occurring on the surface of palladium cathodes during their electrolytic electrolysis in electrolyte on the base of heavy water. The discussion is based on the experimental data on which were obtained in Low Energy Nuclear Reactions (LENR) experiments lead for a number of years in Energetics Technology (Israel) (ET). The results of these experiments were presented in detail at the international conferences on cold fusion (ICCF). The main subject of these presentations was the description of experimental techniques and analysis of the results of calorimetric measurements, which in a number of cases indicated anomalous heat release, sometimes very significant, accompanying the process of electrochemical deuteration of Pd cathodes. However, the processes occurring in the cathode material, in particular, its structural transformations occurring during the absorption of deuterium by palladium, in these reports have appeared practically outside of discussion. This article partially fills this gap and, as the author believes, brings some clarity to the problem of searching for "optimal" palladium cathodes from the point of view of the probability of initiation of LENR.
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1. Introduction

Initial studies of the Low Energy Nuclear Reactions (LENR) phenomenon were carried out in the palladium–deuterium system. Subsequent studies in this direction have revealed a low reproducibility of the effect. The primary task, bearing in mind the low reproducibility of the effect, should be searching for the properties of palladium, which could provide the conditions for its initiation. However, surprisingly little research has been done in this direction. For example, Fleischmann and Pons [1] have indicated that they had used Pd supplied by Johnson–Matthey Company. But by what considerations were guided the authors in choosing this supplier, and what advantages had the metal used by them, have been not specified. Moreover, attempts to detect these properties, undertaken by a number of authors have yielded very insignificant and ambiguous results (see below). As will be seen from the following, the problem posed in this way turns out to be incorrect.

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In a few attempts of this kind, attention was paid to the various physical and structural properties of the original Pd, which used as a cathode in the electrochemical process [2–8].

Similar studies have also been carried out at ET for a number of years. In the course of these studies, it was established that during electrolytic deuteration, a number of processes occur on the surface of the palladium cathode, due to the various causes. Wherein, the metal undergoes complex structural transformations, and the cathode surface significantly changes its relief, and elementary and phase compositions. Some of these processes, as will be shown below, occur very rapidly, starting from the moment of the initial contact of the cathode with the electrolyte.

The result of these studies was the understanding of the variety and complexity of the phenomena occurring on the Pd surface and in the near-surface layer of Pd cathode during its electrolytic deuteration. In addition, the futility of attempts to optimize the properties of the initial Pd with the aim of initiating the LENR became apparent.

2. Experiment and Discussion[a]

2.1. Palladium

The main material for the study at ET was Pd, prepared by a group led by Dr. V. Violante (ENEA, Italy) in the framework of joint work ET with ENEA. In addition, the samples of purity 99.5–99.9% obtained from other sources were used, including the metal supplied by Johnson–Matthey. Details of the experimental procedure used in electrolytic experiments performed by ET are described in [9,10]. It is known, that a palladium produced by various manufacturers and certificated as the metal of high purity, contains a number of contaminants. They can be divided into three types: First type (Pt, Ni, Ag, Ir, Rh, and Au) form with Pd unlimited solid solutions, second type (Ti, Zn, Al, B, Ca, Cr, Fe, Si, Mg, and Si) form the intermediate phases with Pd, and of the third type (e.g., Cu) form with Pd the solid solutions of the various structures depending on their concentrations. It is reasonable to assume that impurities of first type are distributed uniformly in the metal. As for impurities of the second and third types, they form inclusions that have different the electrical conductivity and electrochemical properties. As will be seen from the following, the latter circumstance exerts a strong influence on the process of electrochemical deuteration.

A typical surface appearance of the initial palladium after rolling, vacuum annealing and etching in aqua regia is shown in Fig. 1. Thus structure is typical for palladium samples obtained from various sources. Clearly visible the slip twins (Fig. 1a), formed during rolling, and dark spots (Fig. 1b). The latter are usually located along the rolling direction and are the product of the pyrolysis of the lubricant used in the rolling of the foil during the annealing process. Dark spots are an essential element in the structure of the original palladium and play an important role in the process of electrolytic deuteriation. As can be seen from the data are shown in Fig. 2 and in Table 1, the main supposed phase components of these spots are complex carbides, sulphides, oxychlorides and silicides of potassium, sodium, calcium and aluminium, as well as silicon carbide. The presence of lines of Pd and Pt in the spectrum is due to the participation of the substrate in the formation of the spectrum.

The presence of carbon in all investigated samples, apparently, due to metallurgical factors. Carbon content defined by EDS method, obviously, overestimated, that may be associated with superposition of the spectral lines M_Z Pd (0.286 eV) and K_αC (0.277 eV). The decrease in carbon concentration on the surface of Pd had been observed after metal treatment in glow discharge plasma of deuterium. There are indications that carbon (which, like hydrogen, is an interstitial impurity and occupies octahedral pores in the Pd lattice) reduces the solubility of hydrogen in palladium, and $PdC_{0.1}$ phase suppresses β-PdH formation [11]. Boron additives cause a similar effect.

Carbon, regardless of its origin, plays an important role in the process of electrolytic deuteration of palladium. First of all, it reduces the solubility of hydrogen (deuterium) in the metal. In addition, it leads to the formation of

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[a] Electrochemical experiments were performed by B. Khachaturov, V. Krakov, A. Shapiro, and T. Zilov.
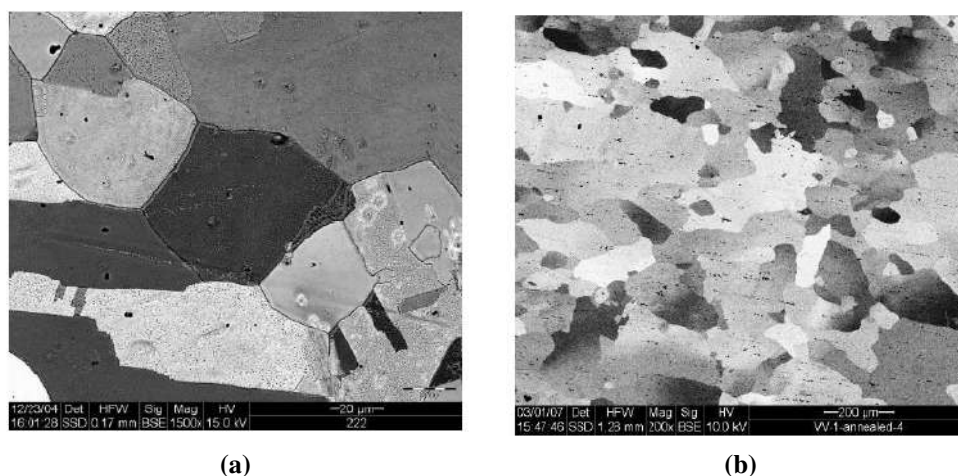
Figure 1. Pd foil after annealing at 850°C and etching in aqua regia, back scattered electrons images. The twins (a) and black spots (b) are seen.

carbide phases of a number of elements - micro-impurities in palladium, for example, silicon, alkaline earth metals, etc. We must also keep in mind the possible interaction of lithium, which exists in the form of various compounds on the surface of palladium, with carbon. The formation of carbide phases on the surface of the cathode is one of the causes of its electrochemical heterogeneity, which plays an important role in the mechanism of deuteration. In this way, micro impurities, forming a micro heterogeneous structure, have a significant effect on the process of electrolytic deuteration [12]. Of course, the mechanism of this influence is different when considering different stages of the process (adsorption, diffusion, recombination, mass transfer, etc.) [13,14].

2.2. Texture

The free energies the faces of Pd (J/m^2) are: (111) – 1.31, (100) – 1.49, (110) – 1.55, and the work functions of these faces are equal (eV) 5.25, 5.11 and 4.87, respectively [15]. Nevertheless, experience shows that the predominant texture of the rolled palladium is (100).

The formation of (100) texture is, apparently, caused by an influence of the impurities (mainly, carbon) at the grain
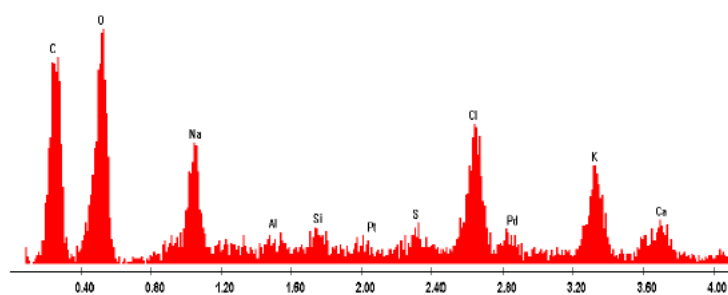

Figure 2. Typical EDS spectrum of the dark spot.

Table 1. The typical composition of the dark spot.

Element	Wt. (%)	At. (%)
C	35.77	52.48
O	26.19	28.84
Na	4.92	3.77
Al	0.43	0.28
Si	1.05	0.66
Pt	0.39	0.04
S	1.44	0.79
Cl	10.68	5.31
Pd	2.55	0.42
K	11.07	4.99
Ca	5.52	2.43
Total	100.00	100.00

boundaries of Pd, which hinder to develop (111) planes parallel to the surface at the rolling procedure. Our experiments on annealing of the rolled Pd in hydrogen convincingly testify to the favor of this assumption. The results of these experiments have shown that the fraction of the texture (111) increases with increasing annealing duration and thus lowering the free energy of the system. Does the texture of the original Pd affect the kinetics of deuterium absorption and (or) to initiating LENR? In [3.5] and other works by the same authors asserted that the texture (100) is the most favorable from the point of view of initiation of LENR. Experimental data are not consistent with this statement. The reasons for this discrepancy are easily understandable. First, besides the texture (100), other orientations, for example (111) and (110), play an important role in initial Pd. The existence of various orientations of grains (and also their sizes!) in the original Pd can be clearly seen in Fig. 3. Secondly, more importantly, during the absorption of deuterium (hydrogen), the intensive processes restructuring of the metal occur, including the reorientation of the grains. This process is especially important in the case of the spinodal decay of the deuterium solid solution in Pd. Finally, the grain boundaries play a much smaller role than the sub-grain ones during the deuterium absorption process. The last two factors will be discussed in more detail below. Therefore, it is not worth to exaggerate the role of the initial palladium texture neither in the processes of adsorption (absorption) of deuterium nor in its initiation of LENR.

It should be noted that deep etching of Pd leads to the formation of the developed microstructures of the type shown in Figure 4, with characteristic prismatic crystals, faceted by the planes (111), very similar to structures spontaneously formed during electrochemical deuteration of Pd. It is clear that such an etching result is due to a decrease in the free energy of the surface. The EBSD method provides valuable information about the orientation of such structural elements, since the X-ray beam in this method falls to the surface at small angles, and the diffraction pattern is formed in a layer several tens of nanometers in thickness. However, the author is not aware of studies of such structures of deep etching of Pd after its electrochemical treatment by this method. Of course, the difficulty of its using it is partly due to the deformation of the metal after the experiment and the formation of an irregular surface.

We used only the X-ray method, in which the depth of formation of the diffraction pattern occurs in a surface layer several microns thick. Therefore, the contribution of surface structures of the type shown in Fig. 4, in the formation of diffraction peaks in this method, is relatively small. The predominant texture (100) of the original palladium samples was detected by us after their standard etching in aqua regia. The textures (111) and (110) have been expressed comparatively weak.

2.3. Grains, mosaic blocks and dislocations

The grain size distributions in some Pd cathodes are shown in Fig. 5. These curves are obtained by using the software "Simagis", developed by Smart Imaging Technologies. It can be seen that the grain sizes practically do not influence
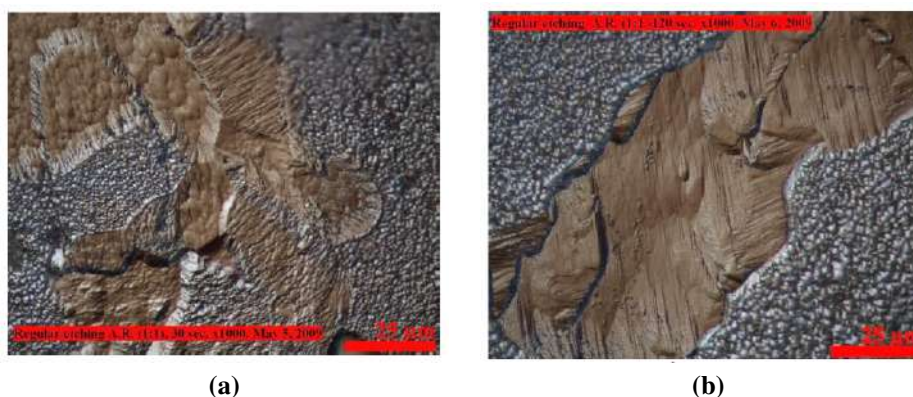
(a) **(b)**

Figure 3. Virgin Pd foils after rolling and annealing at 850°C. Scale bar-25 μm.

the probability of initiation of LENR, and most of the grains have dimensions of ∼50 μm. As noted in [16], such grains are optimal from the point of view of achieving maximum loading.

We measured the sizes of coherent scattering regions (the size of the mosaic blocks) in typical Pd samples by X-ray rocking curve method. They were within the limits of 150–400 nm. Since the boundaries of the blocks of the mosaic are dislocation walls and the latter, it is possible to believe, are traps for absorbed deuterium, it is should be supposed that the grain sizes in themselves do not influence significantly the process absorption, compared to the influence of mosaic blocks' boundaries, bearing in mind that the total length of the latter's approximately three orders of magnitude higher. The typical dislocation density in the Pd sample 64, measured using a transmission electron microscope (JEM 2010) at an accelerating voltage of 200 kV, is ∼3–6 × 10^{10} cm^{-2}.
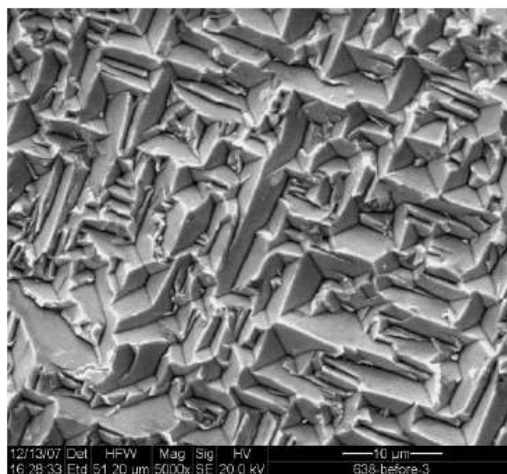

Figure 4. Deep etching reveals the close-packed planes (111) on Pd surface.
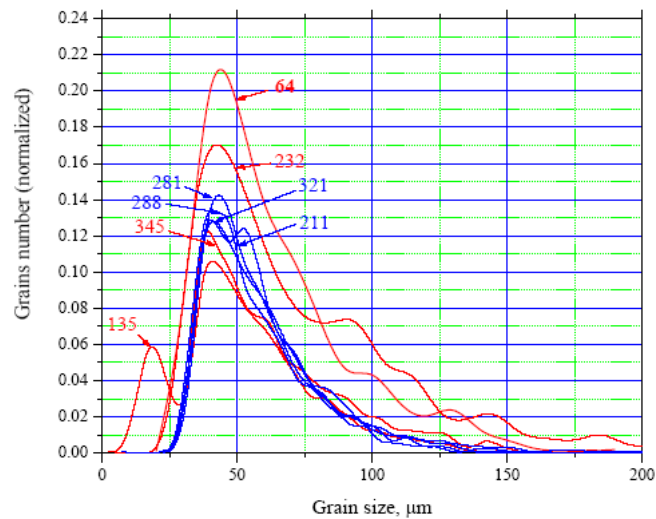
Figure 5. The grain size distribution for some Pd cathodes. The annealing temperature is 870°C, annealing time is 3 h. Red curves – the cathodes showing anomalous heat effect (AHE), blue curves– the cathodes without AHE.

2.4. Spinodal decay

As known [17], the spinodal decay is possible in connection with the system transition into a labile state. This condition is expressed as follows: $(\partial^2\mu/\partial n^2)_{T,P} < 0$. With decreasing this value, the wavelength of the spinodal structures also decreases (Fig. 6). The process is realized by the propagation of a wave of stresses through the sample. The following relaxation of the system gives rise to considerable increasing of the structural heterogeneity. The process is accompanied by so large the increase of defect concentration that their evolution occurs due to the collective effects and formation of the fractal structures. At temperatures below the critical (T_s) at which this condition is fulfilled, the effective coefficient of diffusion, $D(c)$, becomes negative, and the motion of atoms, strictly speaking, can no longer be called diffusion, since it leads to an increase in inhomogeneities. Nevertheless, since Fick's law is formally fulfilled, the diffusion terminology is preserved even at $T < T_s$, and the corresponding atomic transfer for $D(c) < 0$ is known as "upward diffusion". The system relaxation during the spinodal decomposition is accompanied by growth of its heterogeneity. The process is almost non-activated.

In this way as a result of phase transition of β Pd–D solution ($\beta \rightarrow \beta+\alpha$), for example, due to temporarily reversing the polarity of the electrodes, a specific regular modulated structure is formed, whose morphology is determined by the original texture (100) of Pd.

A surprising effect is the difference in textures of newly formed phases: whereas the β-phase texture remains unchanged (100), that of α-phase becomes (110). The result is a significant increase in the concentration of defects, mainly dislocation walls at the phase boundaries, a/β, and $\beta \leftrightarrow \beta+\alpha$ decay is accompanied by profound rearrangement of Pd–D solid solution, leading to a significant increase in the dislocation density (up to 10^{11}–10^{12} cm^{-2}).

2.5. Electrochemical heterogeneity of the Pd cathode surface and its consequences

So, the dispersed two-phase structure forms when the spinodal decay of β solid solution Pd–D occurs. It is important for us is the difference of the potentials of these phases in equilibrium with the electrolyte.
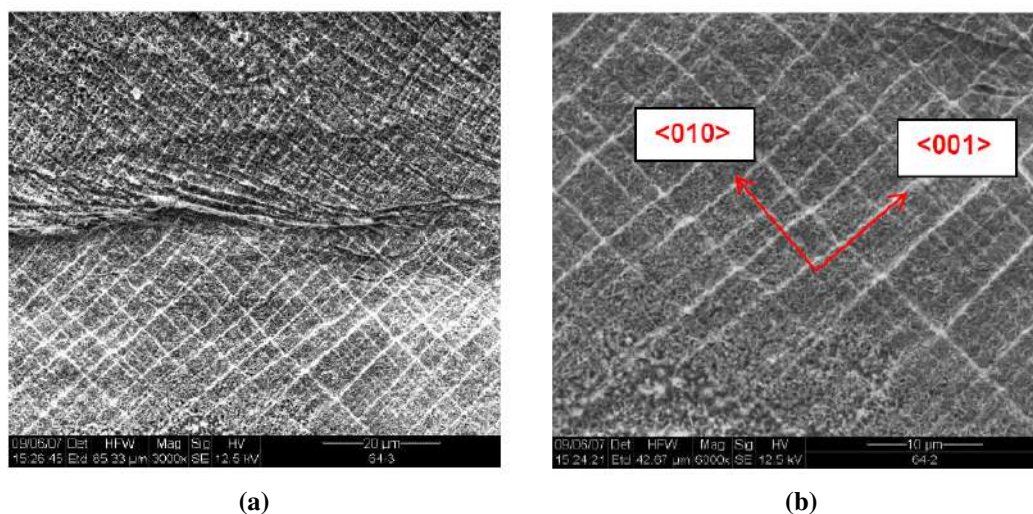
(a)   **(b)**

Figure 6. The spinodal decay of β phase (Pd–D solution) and formation of the hierarchical multi-level structures. This extremely heterogeneous structure consists of β and α Pd–D solid solutions. The dislocation walls confine rectangular sub-grains.

According to [18], the open circuit voltages (OCV) of α and β phases relative Pt reference electrode is equal to –0.85 and –1.35 V, respectively. Unfortunately, in the literature, there are no data on the measurement of the electrochemical heterogeneity of the surface of the Pd cathode during its electrochemical deuteration, for example, at the simultaneous presence of α and β phases. At the same time, such in-situ measurements, for example, using the scanning reference electrode technique (SRET), and the scanning Kelvin probe (SKP) [19–23], would make some clarity regarding the details of adsorption, absorption, and surface mass transfer mechanisms of the electrochemical deuteration of Pd. Thus, the scanning Kelvin probe force microscope gives good spatial resolution at direct measurement of the local Volta potential differences resulting from very complicated microstructures. These studies are particularly important since the heterogeneity of the surface of the Pd cathode is its immanent property and decisively influences the mechanism of the process.

The electrochemical heterogeneity of the Pd surface can be caused not only by the spinodal decay of the β Pd–D solution but also by the presence of the other inhomogeneities, for example, the dark spots, the secondary palladium crystals growing in the process of electrolysis with a content of Pt lower than on the rest of the cathode surface, etc. In addition, it must be borne in mind that the original Pd always has foreign, often poorly conducting inclusions, which have a metallurgical origin. We observed various types of similar inclusions, for example, Quartz, silicates, and alkali metal aluminates, etc. It should also be mentioned formation, during the electrolytic process, of the halides, carbonates of the alkaline and alkaline earth metals, localized, as a rule, on the protrusions and facets of newly formed crystals. One should not forget about the presence of Li on the surface of the cathode, which forms solid solutions, inter-metallides and multi-component compounds with the impurities contained in Pd. We detected Li, in particular, in the form of lithium aluminate by the X-ray method. A presence of all these types of micro impurities on the surface, as our experience shows, is almost inevitable, especially when working with open cells.

Thus, the complex elemental and phase compositions of the Pd cathode with heterogeneity of different compositions and sizes, up to submicroscopic ones, create a complex distribution of the electric potential on its surface during the electrochemical process. Finally, a specific contribution to the electrochemical heterogeneity of the surface is introduced by its uneven relief due to the plastic deformation of the metal, because the potentials of the protruding areas

and depressions on the cathode surface are different [24]. Thus, a complex distribution of electrochemical potentials arises on the surface of the Pd during its cathodic polarization, accompanied by the appearance of surface currents and, consequently, surface mass transfer. In this case, relatively non-noble (having a more negative potential relative to the matrix) surface areas, can dissolve in the surface layer of the electrolyte. The reverse process occurs on relatively noble areas. The rates of these processes depend on the magnitude of the local electric fields.

In our experiments, we observed an almost equilibrium "growth" of negative Pd crystals in the form of a truncated semi-octahedron on grains with orientations (100) and (111) – (Figs. 7a and b, respectively) and fast growth of secondary dendritic Pd crystals (Fig. 7c). The growth of dendrites, as a rule, occurs in places of localization of electric fields of high intensity arising at the boundaries of a conducting matrix with non-conducting inclusion. Usually, we observed the growth of such dendrites in places where dark spots were located (Fig. 7c). Often spatially separated dissolution–crystallization processes occupy significant areas of the cathode surface, and in that cases we observe vast surface areas, with characteristic etch structures and mass secondary growth (Fig. 8). A striking similarity is found between the structures of the initial etched palladium (Fig. 4) and the extensive surface sections of the Pd cathode after its electrochemical deuteration (Fig. 8a and c). Figure 8c presents a remarkable picture of the mass crystallization of secondary Pd crystals with a highly developed lace-like structure and an increased content of Pt. It is clear that the description of structures of this kind in terms of their texture does not make sense.

2.6. About selection criteria for Pd cathodes

From what has been said above, it is easy to conclude that the search for properties of the initial Pd that would contribute to the initiation of LENR is meaningless since both the composition of the metal surface and its structure undergo significant and rapid changes immediately after the beginning of the electrochemical process. It must be assumed that this circumstance caused the ineffectiveness of such attempts. Certainly, and our attempts to find correlations between the various physico-chemical and structural characteristics of the original Pd and the probability of nuclear transformations also turned out to be futile.

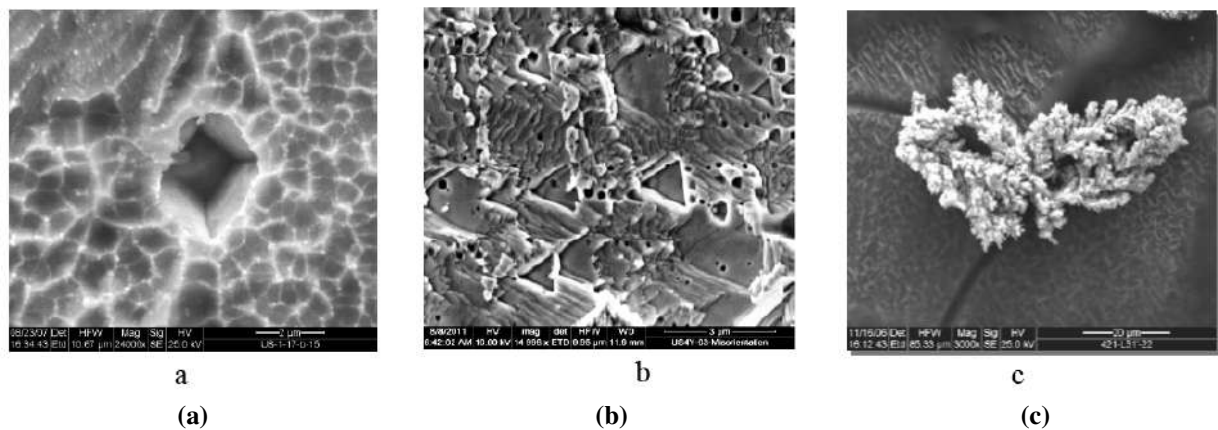Let us look at the most popular assumptions about these criteria.

(a)　　　　　　　　　　(b)　　　　　　　　　　(c)

Figure 7. Growth of the negative and the secondary Pd crystals on Pd cathode during electrolytic deuteration; a, b-the negative crystals grown up on the Pd grains of the $\langle 100 \rangle$ and $\langle 111 \rangle$ orientations correspondingly, c – the dendritic secondary Pd crystals grown up on the Pd-dark sport boundary.
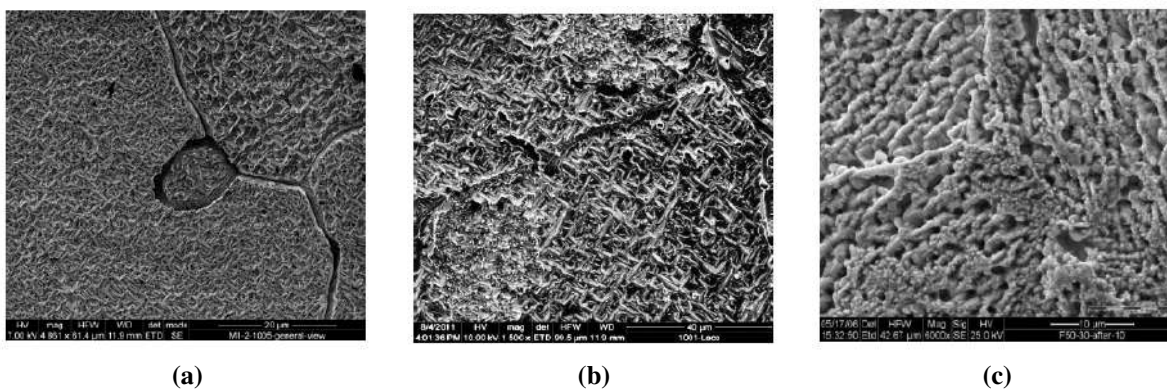
Figure 8. Structural transformations of the cathode surface; a) and b) - apparently, the cathodic regions, undergone the etching process; (compare to the structure shown in Fig. 4, c) a mass crystallization of the secondary Pd crystals (compare to Fig. 7c).

(a) Common is the assertion that the probability of LENR increases with increasing ratio D/Pd, especially at its values more than 1 [2,25, 26]. Although the D/Pd parameter has an indirect relationship to the search for palladium estimation criteria, its discussion is of great methodological importance. The fact is that the experimental data obtained in different laboratories are contradictory.

Thus, the probability of AHE, according to [26], increases with the increasing in the concentration of deuterium in Pd, and the probability of AHE increases sharply as the loading approach approaches 1. At the same time, in accordance with the data obtained by ET, the effect was observed usually at D / Pd ratio 0.6–0.7, i.e. near the phase boundary of $\alpha + \beta/\beta$. Similar results have been obtained by Storms [12]. From general considerations, it is clear that the probability of the interactions of deuterons, leaving aside the problem of overcoming the Coulomb barrier, does not require extremal high average concentrations of deuterium absorbed in the metal. It is reasonable to assume that a high local concentration of deuterons, say, on dislocation walls, is quite sufficient incentive to initiate their interaction. Anyway, any of known models LENR does not give a reasonable explanation of sharp increase of probability AHE at extremely high loadings which are coming close to 1.

Thus, this problem requires additional theoretical and experimental studies, taking into account other process parameters, for example, the temperature of the cathode and the duration of the incubation period.

(b) Both characteristics of the initial Pd, namely, texture and grain sizes are very popular as quality parameters of the metal. Supporters of this idea tacitly assume that the loading values play a significant or even dominant role in initiating the LENR (see point a). However, even if we accept the high loading postulate as a prerequisite in initiating LENR, then these parameters cannot play a significant role since radical changes in the surface structure and the formation of a developed sub-grain structure of the metal during its cathodic polarization make their optimization meaningless. From the foregoing, it is also obvious that the statement about the favorable role of the texture (100) as concerning fast loading, and, consequently, the initiation of the LENR effect, does not have any grounds.

As for the influence of the grain size, the foregoing consideration indicates clearly that this parameter does not have any effect on the initiation of the effect and therefore cannot serve as a criterion for Pd pre-selection. First of all, direct experimental data contradict this position (see Fig. 5). The inapplicability of this criterion is obvious, bearing in mind that it is the sub-grain, and not the grain structure, that plays an important role in the absorption of deuterium. In

fact, if we assume that the increase in time of settled life of the absorbed deuterium ions and, therefore, the probability of interaction of their nuclei associated with the concentration of dislocations as traps for deuterium ions, then just the sub-grain structure can be a parameter to optimize the structure of the original Pd.

(c) In the papers of V. Violante with co-workers (see, e.g. [2,8]) the measurements of the surface energy spectra of the Pd, or a specific state of the surface of the metal, e.g., its roughness, the spectra of the surface plasmons, the form of the power spectral density function, etc., have been suggested as criteria the probability of the LENR. In a view of the aforesaid apparently, that cardinal restructuring of a surface of metal during its electrochemical processing changes a type of the specified spectra right away after the beginnings of experiment and renders impossible to accept such measurements as a way of preliminary selection of cathodes.

It is this circumstance that is the reason why it is impossible in principle to develop criteria for estimating the initial Pd in view of achieving the reproducibility of the LENR effect.

3. Conclusions

The foregoing considerations lead us to a conclusion that there are no properties of the original Pd, the optimization of which could trigger the LENR mechanism automatically due to the high stochasticity of the electrochemical system. Therefore, we have to reformulate the problem. First, it is necessary to achieve reproducibility of the experiment. That is, to exclude, or at least minimize the influence of uncontrolled parameters. The main factor that introduces uncontrollable disturbances into the system is the presence of micro-impurities in Pd. Therefore, the first step in overcoming the low reproducibility of the experiment is the use of high-purity metal. Here we can see an obvious analogy with the beginning of the semiconductor era. An essential flaw in this analogy is the absence of the working theory of LENR. The existence of such a theory would radically change the formulation of the problem, namely, instead of improving reproducibility, the task would be a programmable launch of LENR.

The difficulty in obtaining pure Pd is caused its high absorption capacity with respect to the interstitial impurities. Therefore, a promising direction should be considered making of film cathodes by Pd deposition on metal substrates in reducing environment or in high vacuum.

When preparing compact Pd cathodes, one should be guided by the following considerations: (1) dealing with a pure metal containing minimum impurity content; (2) the annealing parameters do not play a decisive role and should be selected only from the consideration of minimizing the internal stresses in the metal arising during its rolling.

Preliminary oxidation of the cathode should be carried out in pure oxygen. The metallurgical cycle and subsequent metal treatments (rolling, etching, etc.) should be carried out in clean rooms. It would be reasonable to process Pd foils after rolling or after annealing by glow discharge plasma of the deuterium with the purpose of getting rid of lubricant residues.

Obviously, it is necessary to refuse to work with the open electrochemical cells, though they show sometimes outstanding, but highly irreproducible results with respect to AHE.

Acknowledgements

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